62-3-1

AFCRL - 62-156

The Travelling Solvent Method of Crystal Growth

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Project 4608
Task 46088

Quarterly Report #3

Covering Period November 15 thru February 15, 1962

Contract No. AF 19(604) 8803

Prepared for:

Electronics Research Directorate
Air Force Cambridge Research Laboratories
Office of Aerospace Research
United States Air Force
Bedford, Massachusetts

March 8, 1962

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Introduction

During this report period work has been carried out in the following areas:

Ga-GaAs System

(1) Characterization of the zone movement process.
Study of variables such as temperature, temperature gradient, zone thickness and surface preparation.

(2) Evaluation of regrown GaAs by Van de Pauw disc technique.

(3) Preparation of ohmic contacts to GaAs

Si-SiC System

(1) Construction of a radiant heating zone passing furnace.

(2) Deposition of thin zone of Cr from chromium dicumene.

(3) Preparation of ohmic contacts to SiC.

The Gallium Arsenide-Gallium System

Work has continued this Quarter on the determination of the optimum conditions for the zone movement of liquid Ga through GaAs. Such variables as temperature, temperature gradient, zone thickness and surface preparation have been investigated.

Characterization of the movement has been difficult since this particular type of experiment does not lend itself easily to accurate analysis, particularly in the area of temperature measurement. In the following discussion the results of several zone passing experiments will be described, with emphasis on a general characterization of the zone movement process.

The preparation of the GaAs-Ga sandwich has been carefully evaluated since initial zone movements gave erratic results. In some cases extremely large amounts of Ga were found to have passed through the GaAs single crystal, and in others the liquid Ga was hardly noticeable. Since the thickness of the Ga zone is critical both in zone movement efficiency and in the desired analysis of the Ga+GaAs region of the phase diagram, it was desirable to elucidate this anomalous behavior. After careful examination it became apparent that much of the trouble stemmed from the inaccuracy of the sandwich making equipment. A new sandwich apparatus designed with smaller tolerances, has functioned much more satisfactorily. All final observations of zone thickness have correlated well with the original amount of Ga introduced. Best results have been obtained with liquid gallium zones of one mil thickness. Thicker zones bring about undesirable convective stirring effects in the liquid. Thinner zones obviously limit the obtainable temperature gradient. Further evidence will be necessary before we can make a more specific analysis of this question.

The determination of the actual temperature gradient was also given some study. One experiment was performed to determine the temperature gradient as a function of temperature range.

Two chromel-alumel thermocouples in contact with the upper and lower sections of a GaAs disc were used to indicate the temperature. Alloying of the GaAs with the thermocouples was observed. The error in

temperature measurement caused by this alloying was small as indicated by subsequent measurements in known temperature environments. The results obtained are given in Table I.

Table I Temperature Gradient in Ga-GaAs Sandwich (100 mils)

Heater Temp. ^{o}C	Top Temp. ^{o}C	Bottom Temp. ^{o}C	T
765	588	410	178
975	821	622	199
1250	1095	914	181
1327	1147	984	163

The bottom temperature is monitored during each zone movement experiment. It has been found that significant movement is not observed below approximately 800^{o}C regardless of the temperature gradient. Above this temperature the rate of zone movement appears to be independent of temperature. It should be kept in mind that the experimental pyrometry is complicated by the radiation type heating system. The top temperature may actually be much lower than the observed temperature. Assuming a straight line temperature profile (no thermal contact resistance) the gradient across the liquid gallium zone is probably 2^{o}C. The apparent rate of zone movement is 20 mils/hr.

Experimental Results

X-Ray analysis verified the single crystal nature of the regrown GaAs crystals. Spiking or excessive solution rates along highly strained regions (imperfections) has, in some cases, broken up the liquid Ga zone. This process may complicate zone movement through polycrystalline GaAs; however, in this case an averaging process may stabilize the Ga-GaAs interface.

The feasibility of producing stacked structures of various GaAs slices was investigated by placing a separate slice of GaAs, "A" face down, on top of the Ga-GaAs sandwich. The cross section of the produced crystal is shown in Fig. 1. The liquid Ga zone passed up through both sections of GaAs leaving behind fairly sharp junctions. In this crystal however, structures characteristic of stray crystals, subgrain bound-

aries or, more likely, chemical inhomogeneities appeared adjacent to, and grew through, the second interface. These may have been caused by irregular temperature profiles in the lower crystal as a consequence of the inevitable gap between the upper GaAs slices.

Evaluation of Regrown GaAs:

Disc Hall and Resistivity Measurements

The measurements of specific resistivity and Hall coefficient of the regrown GaAs crystals has been accomplished by the technique first described by Va de Pauw[1]. This technique facilitates the electrical characterization of small discs of arbitrary shape; therefore, it is most suitable to the particular system in question.

In this method four ohmic contacts are placed on the circumference of the crystal as shown in Fig. 2.

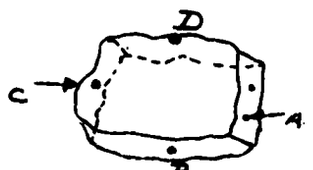


Fig. 2.

The specific resistivity and Hall coefficient of the crystal can be measured without knowing the current pattern if the following conditions are fulfilled:

a) contacts are at circumference of the sample.
b) contacts are small.
c) sample is homogeneous, and of uniform thickness.
d) surface of sample is singly connected; no isolated holes.

The specific resistivity may be obtained from the following expression:

$$\rho = \frac{\pi t}{\ln 2} \frac{(Rab, cd + Rbc, da)}{2} f\left[\frac{Rab, cd}{Rbc, da}\right]$$

where Rab, cd is the voltage drop measured across contacts c and d when

current flows across a path from a to b. (The first two letters denote the current leads and the second two denote the voltage leads).

t = thickness of the sample

and $f\left[\frac{Rab,\ cd}{Rbc,\ da}\right]$ is a function which satisifes the relation:

$$\frac{Rab,\ cd}{Rab,\ cd\ +\ Rbc,\ da} = \text{arc cosh}\left(\frac{\exp\ \ln\ 2/f}{2}\right)$$

If the contacts are positioned symetrically, Rab, cd and Rbc, da are almost equal, therefore the f may be approximated by

$$f \approx 1 - \frac{Rab,\ cd\ -\ Rbc,\ da}{Rab,\ cd\ +\ Rbc,\ da}^{2}\ \frac{\ln 2}{2}\quad \frac{Rab, cd - Rbc, da}{Rab, cd + Rbc, da}^{4}\ \frac{\ln 2^{2}}{4}\ \frac{\ln 2^{3}}{12}$$

The Hall mobility (μ_h) may be obtained from the following relation

$$\mu_H = \frac{t}{B}\quad \frac{\Delta\ Rbd, ac}{\rho}$$

where t = thickness

B = magnetic intensity in gauss

ρ = resistivity

Δ Rbd, ac is the change in voltage drop across AC when a magnetic field is impressed perpendicular to the surface of the crystal.

Preparation of Contacts

Low resistance ohmic contacts are required for the measurements of specific resistance and Hall mobility. As previously mentioned, the position and size of the contacts are of utmost importance in the Van de Pauw analysis.

Various contact materials and techniques were studied. The results and observations are listed and discussed below.

(1) Fine gold wires (5 mils in diam.) were pulsed into GaAs by the passage of A. C. current. This technique was not suitable for high resistivity GaAs (1 Ω-cm) since the high contact resistance did not allow sufficient current to flow. The brittle nature of these contacts made it virtually impossible to place four symetrically spaced contacts on the same crystal.

(2) Fine gold wires(5 mils in diameter) were alloyed into an etched GaAs surface heated to 600°C in argon. Four symetrically spaced contacts were made simultaneously in this technique. However, the gold wire would become detached from the GaAs when alloying took place. Soldering to the Au-GaAs alloy contact met with only limited success.

(3) Successful contacts were obtained using pure indium in conjunctions with the quartz positioning jig shown in Figure 3. The technique involved the melting of pure In into the four channels of the quartz jig in pure argon at 550°C. Perfectly aligned low resistance ohmic contacts, approximately 10 mils in diameter, were obtained in this manner. Since the entire quartz jig was placed in the magnetic field, the problem of contact breakage was not encountered.

The error in Hall mobility ($\frac{\Delta \mu_H}{\mu_H}$) produced by a finite contact size is illustrated in the following example.

Assume A=B=C= 10 mils

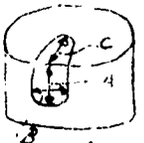


Figure 4.

For small values of t D, the error in Hall mobility is as follows:

A direction: $\frac{\Delta \mu_H}{\mu_H} = \frac{-2d}{\pi^2 D} = 0.005$

As a first approximation, since there are four contacts; error = 2%

B direction $\frac{\Delta \mu_H}{\mu_H} = -\frac{4d}{\pi^2 D} = 0.010$

since 4 contacts; error = 4%

C direction $\frac{\Delta \mu_H}{\mu_H} = -\frac{2d}{\pi D} = 0.0167$

since 4 contacts; error = 6.68%

Error in C direction not present in this study, therefore a conservative estimate of the contact size error in mobility $= \frac{\Delta \mu_H}{\mu_H} = 6\%_2$ for 10 mil diam. contacts.

Results of Evaluation

Table II shows the excellent agreement between results obtained by the normal parallelepiped technique and the disc Van de Pauw technique. The difference in Hall mobility obtained by the two techniques is within the usual limits of error.

Table II also shows that the GaAs crystal, TLI #1, had a higher specific resistivity and Hall mobility after regrowth. This indicates that some type of purification phenomenon took place during zone movement. The crystal remained "N" type (determined by the hot probe technique) which is surprising since Ga is known to be a "P" type dopant in GaAs.

Compensation processes may therefore be the cause of the observed increase in specific resistivity.

TABLE II

Electrical properties of original and regrown GaAs

Type	Sample	Specific Resistivity (ohm-cm)	Hall Constant R_H (cm^3/coul)	Carrier conc. C (Cm^{-3})	Hall mobility μ_H (cm^3/v-sec)
N	Wacker Normal tech.	0.1	560	1.12×10^{16}	5,600
N	Wacker Van de Pauw	0.097	498	1.26×10^{16}	5,140
N	TLI #1 Initial	0.014	33.5	1.86×10^{17}	2,450
N	TLI #1 Regrown	0.061	210	2.97×10^{16}	3,420

The SiC-Cr System

The major problem encountered thus far has been in the construction of a furnace which could withstand the severe temperature limitations imposed by the melting point of chromium (1890°C). The apparatus described in the previous Quarterly report, while capable of withstanding these temperatures for a short duration, could not be used for extensive periods due to the devitrification of the quartz tube. Attempts to use molybdenum heat shields were successful; however, the shields were extremely difficult to position. In an effort to give as much versatility to the system as possible, a new apparatus has been designed and is now being used. This system uses a strip heater of tungsten or graphite which is heated to 2300°C. The heater radiates to the silicon carbide sandwich producing both the requisite temperature, and temperature gradient. In many ways the present apparatus is very similar to that being used in the gallium arsenide study.

Power is supplied by a 500 amp, 20 volt C. T. transformer which is controlled by a 10. 8 KVA single phase ganged variac. The temperature of the heater is measured by an optical pyrometer, and the temperature of the bottom of the sandwich is measured by a tungsten-rhenium thermocouple which is in contact with the beryllia disc. This thermocouple is calibrated, and is operable to 2700°C. Figure 5 shows the experimental strip furnace.

Deposition of Chromium

Previously, chromium has been lapped or ground to the required size and then assembled in the sandwich. While this technique can be used, it is far from ideal. The sandwich usually moved somewhat and unless the three pieces (2 SiC, 1 Cr) were perfectly flat, the assembly tended to separate. In addition, lapping or grinding of chromium to a one mil thickness was rather tedious.

Two alternatives immediately suggested themselves; (1) electroplate chromium onto the silicon carbide, or (2) deposit the chromium from the vapor phase. The present effort has been directed toward the deposition of chromium by the thermal decomposition of chromium dicumene.

Chromium from chromium dicumene

Chromium dicumene is a toxic liquid which has an appreciable vapor pressure at 200°C, and decomposes above 300°C. A simple apparatus has been constructed which will be used to deposit chromium on silicon carbide slices. Figure 6 shows the apparatus. It consists of a glass chamber which is heated to the proper temperature by two separate heating tapes. The system is evacuated and flushed several times before heating. A carrier gas such as nitrogen or helium is passed over the chromium dicumene at 200°C. The dicumene is then carried to the hot section of the chamber, which is maintained at above 300°C, where it decomposes and deposits chromium on the silicon carbide. The spent gases are then exhausted.

Grinding of Silicon Carbide

A new technique for the preparation of silicon carbide chips was suggested in a discussion with Mr. E. D. Porter et al of Norton Company, Chippawa, Ontario. They suggested the use of an ultrasonic impact grinder to lap the surface of the silicon carbide chips. An ultrasonic lapping tool has been prepared and this method of forming the silicon carbide will be attempted.

Preparation of Ohmic Contacts to Silicon Carbide

Low resistance ohmic contacts are necessary in order to perform Hall measurements on silicon carbide by the Van de Pauw method. An intensive literature survey revealed several methods for making ohmic contacts to silicon carbide. The method that appears to be particularly suited to the present work, an electroless nickel technique, is discussed by Richard L. Raybold of the National Bureau of Standards in Technical Report No. 1, AFCRC-TN-59-999, December 1, 1959. This method had to be modified by the inclusion of a sintering step as described below:

1. Lap the silicon carbide surface with a slurry of 6 micron diamond paste and acetone.
2. Soak in 30% HF-70% HNO_3 for a few minutes.
3. Clean in boiling isopropanol.
4. Anodically etch in HF
5. Rinse in distilled water.
6. Sensitize by dipping in a bath containing 10% stannous chloride.

7. Rinse in distilled water.
8. Dip in palladium chloride solution (0. 2%).
9. Rinse in distilled water.
10. Dry with a blast of dry N_2.
11. Plate for about 1 minute at about 90°C.
12. Ultrasonically clean.
13. Sinter for 20 minutes in hydrogen at 840°C.

The composition of the plating solution is:

$NiCl_2$: 6 H_2O	30 g/l
NaH_2PO_2:H_2O	10 g/l
$NaC_2H_3O_3$	50 g/l

By careful handling, excellent ohmic contacts have been prepared.

Summary

Even though early experiments on the zone-passing of chromium through SiC have verified the essential validity of the concept of TSM, numerous experimental difficulties have been encountered in achieving systematic and reproducible results. Progress towards solving these difficulties has been made in all areas. We are confident that the main interest of the program, i.e. a study of the Cr-SiC system as such, can now be exploited without further diversions. Although simpler and less controllable techniques for studying this system could have been employed, we feel that the approach actually taken will be vindicated by the more reliable data which will result.

Future Plans

I. Ga-GaAs system.

1. Continue work to determine Ga-GaAs phase diagram in region of interest.
2. Design apparatus and initiate experimentation on Peltier movement using polycrystalline and single crystal GaAs.
3. Preparation and evaluation of rectifying junctions.

II. Si-SiC system.

1. Determine effect of temperature, temperature gradient and zone thickness on zone movement.
2. Evaluation of regrown SiC by Van de Pauw technique.

III. Preparation of ZnTe and GaP in suitable form for use in zone movement experiments.

Figure 1. Cross section of regrown GaAs. Etched in $3HNO_3$: 1 H_2O 20X

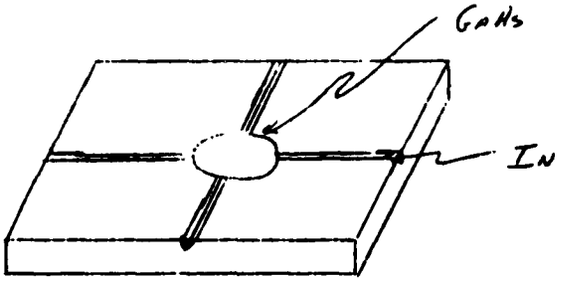
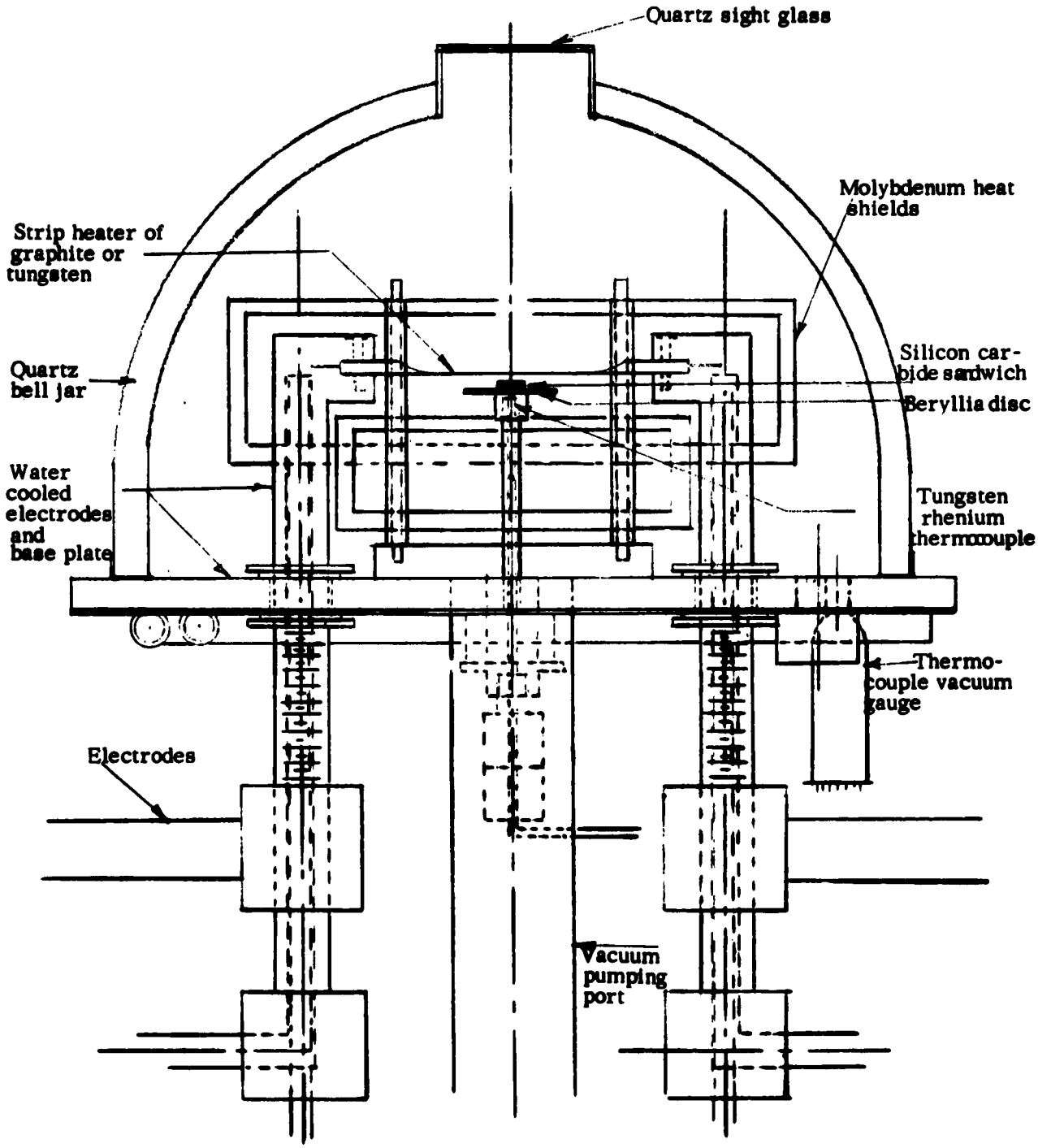


Figure 2. Quartz positioning jig.

Figure 5. Schematic Diagram of Experimental Strip Furnace



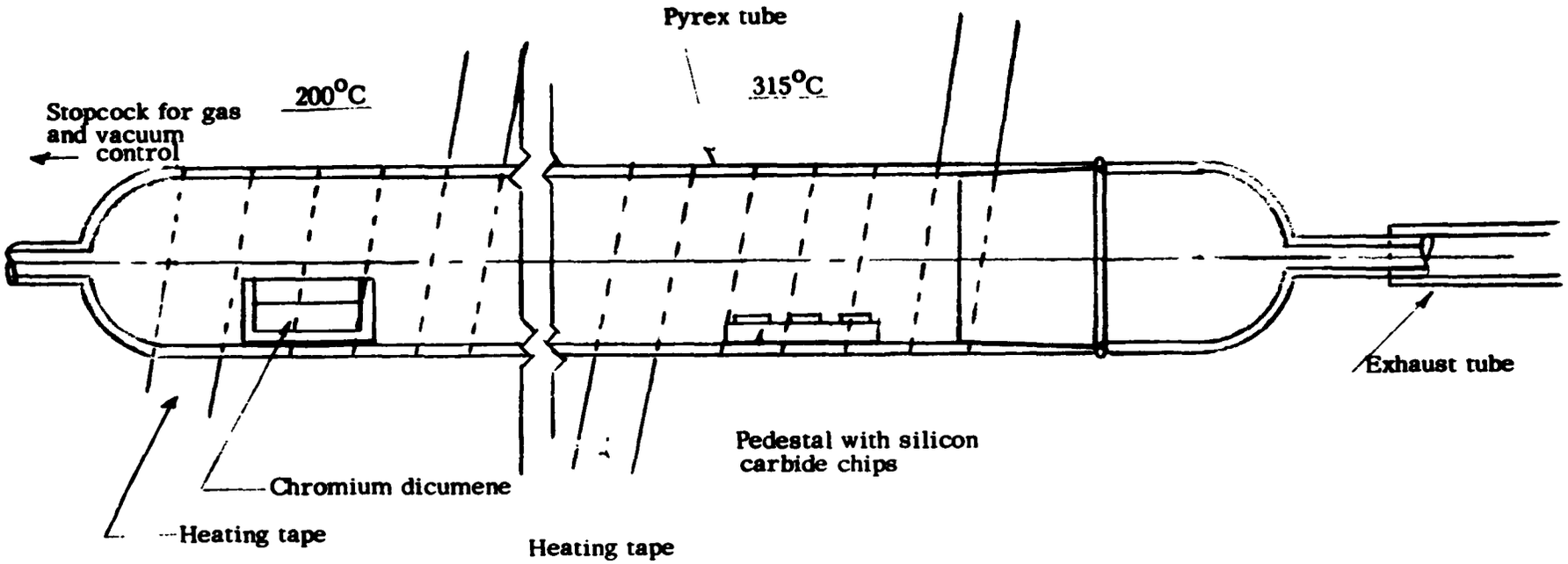


Figure 6. Experimental arrangement for deposition of chromium from chromium dicumene.